

THE PERMIAN-TRIASSIC BOUNDARY IN AUSTRALIA: WHERE IS IT AND HOW IS IT EXPRESSED?

C. B. FOSTER, G. A. LOGAN & R. E. SUMMONS

Australian Geological Survey Organisation, PO Box 378, Canberra, Australian Capital Territory 2601, Australia

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Placement of the Permian-Triassic boundary in Australia, and particularly in Queensland, relied initially (1950s) on lithological criteria. The boundary was taken as coincident with the change from coalmeasures (Permian) to non-coaly sediments, principally redbeds. This was, and remains, a convenient field and subsurface mapping point. Subsequently, palaeontological evidence (1960s) focussed on the demise of the *Glossopteris* Flora as a marker for the upper boundary of the Permian System. Palynological studies (1970-90s), linking at least broadly to the macrofloras, and, most importantly, to palynofloras from the independently dated Salt Range section, indicated that a major floral change which began during the close of coal measure sedimentation, was of early Changhsingian age. The interpretation is necessarily dependent on stratigraphic range data from the Pakistan section, and on establishing migration pathways for the parent floras. The almost global appearance of monolete, sculptured, cavate lycopod spores of *Aratrisporites*, which first appear in the non-coaly sediments, above the last Permian coal seams in eastern Australia, and in faunally dated Early Triassic (upper Greibachian) sediments in western Australia, has been suggested as a marker for the basal Triassic. But acceptance of this criterion is not agreed by all workers.

SHRIMP (Sensitive High Resolution Ion Microprobe) dating of single zircons from the type Meishan section, China, has provided a numeric age for the P-T boundary (based on the appearance of the conodont *Hindeodus parvus*) of about 252 Ma. SHRIMP dates of tuffs from eastern Australia, occurring several hundreds of metres below the base of the coalmeasures have been dated at 251 Ma, which if correct would infer that the coals were of Triassic age! However, these ages have been established using different zircon standards, and the standard used for eastern Australia seems to give younger ages. This problem is under intensive investigation, and so, at present, SHRIMP does not provide a boundary solution.

Changes in carbon isotopic composition of organic matter have been suggested as a proxy for the boundary in Australia. But these criteria too, are imprecise, as the origin of the organic matter effects the value of the isotopic composition; such that woody derived kerogen is isotopically heavy (-24‰) and nonwoody kerogen is consistently lighter (to -32‰). The resultant signature reflects constraints imposed by admixtures of organic matter, biofacies, and depositional history. A lack of carbonates at the P-T boundary in Australia precludes the use of carbon isotopes from this source.

The problem of recognition of the P-T boundary in Australia, and in Gondwana in general, is exacerbated by rarity of marine index fossils, in particular conodonts, so that correlation with the marine standard sections of the warmer northern hemisphere deposits is not possible.

After 25 years, the P-T boundary in Australia remains elusive and between two anchor points of Late Permian (but not latest) and late Early Triassic age. Correlation with the Late Permian (early Changhsingian) uses palynological criteria in eastern Australia, and the late Early Triassic is defined by marine faunas in western Australia.

THE CLOSE of the Permian has remained an emotive issue since the contemporary extinction of much of the marine fauna, about 250 million years ago, until the present. Global catastrophe caused either by the destabilisation of gas hydrates and consequent flooding of the world's atmosphere with methane, or over turn of stagnant deep ocean waters are among the current explanations for the demise of the marine fauna (see Erwin 1993, 1994; Knoll et al. 1996). In many parts of the world, the rock record shows evidence of a severe

Late Permian regression which exposed marine shelf areas, followed by a widespread transgressive event in the Early Triassic. These events have been correlated using evidence from rock and fauna deposited in marine environments, although traditionally, the uppermost stage of the Permian System, Tatarian Stage, is based on the non-marine rocks of the Russian Platform. Correlation with the Russian section has relied on plant megafossils and plant microfossils (spores, pollen, algae, ?fungi), insects, and conchostracans (Figs 1, 2).

TIE POINTS	EASTERN AUSTRALIAN BIOZONES	PALYNOLOGY FAD	STYLISTED GEOLOGY (QLD)
Upper Lower Greisbachian	<i>Kraeuselisporites saeptatus</i>	<i>Aratrisporites</i>	Rewan Group
	<i>Protohaploxylinus samolovichii</i>		No coal
	<i>Lunatisporites pellucidus</i> APT1	<i>K. saeptatus</i>	Red beds
?	<i>Protohaploxylinus microcorpus</i> APP6	<i>R. foveolata</i>	<2000 m
	<i>Playfordiaspora cancellosa</i> APP6	<i>Chordecystia</i>	
Lower Changhsingian	Upper Stage 5	<i>P. cancellosa</i>	Coal Measures
	(<i>Glossopteris</i> Flora, GF)	<i>T. playfordii</i>	(100 m-400 m)
251±	APP5	<i>D. parvithola</i>	Last marine sediments <900 m
	Lower Stage 5 (GF)	APP4.3	Marine <700 m
			non-marine tuffaceous not to scale

Fig. 3. First appearance datums (FADs) of key plant microfossils, and their correlation with faunally recognised tie points in WA, and the Salt Range of Pakistan. Stylised geological column shows typical sediment thickness over this interval in the Bowen Basin, Queensland.

tuffs within the Changhsingian have been dated using SHRIMP (Sensitive High Resolution Ion Microprobe) and Ar/Ar methods. Carbon isotopes from both carbonates ($\delta^{13}\text{C}_{\text{carb}}$) and the organic matter ($\delta^{13}\text{C}_{\text{org}}$) from within the section have also been studied and reported on extensively. A marked shift to isotopically light carbon has been suggested as a proxy to mark the boundary between the Changhsingian and the Triassic.

In Australia, Late Permian marine deposits are rare, and none appear to be as young as the Changhsingian; the youngest faunas are of Dzhulfian age, and confined to the Canning and Bonaparte Basins (Archbold 1998). Permian conodonts, because of cool water conditions, are rare and known only from the Early-Middle Permian of Western Australia. *H. parvus*, the Triassic index has not been found in Australia. Marine fauna from the Perth Basin, Kockatca Shale, provide an international tie with part of the Griesbachian, the oldest Stage of the Triassic. Because of the lack of fauna, correlation with the standard sections has been through palynology, and more recently, using proxies for the P-T boundary: SHRIMP dates and isotopic signatures from kerogen ($\delta^{13}\text{C}_{\text{org}}$).

The purpose of this paper is to provide a succinct overview of the available evidence for placement of the P-T boundary in Australia.

LITHOLOGICAL CRITERIA

There is a distinct lithological change between coalbearing sediments of the Baralaba Coal Measures and the overlying, non-coaly, often red-

bed, sediments of the Rewan Formation in the Bowen Basin of Queensland (Fig. 3). Geologists of Shell Development Pty Ltd (1952) selected this convenient field mapping surface as the boundary between the Permian and Triassic, although at that time there was no palaeontological supporting evidence for this decision (Hill 1957). In subsurface studies, the first downhole occurrence of either coal seams or highly carbonaceous sediments was taken to mark the upper boundary of the Permian. Again this is a convenient, recognisable mapping point, but it does not take into account any erosion that may have occurred, and the assumption that the first downhole coal seam is the youngest of the coal measures is not always correct. Similarly the uppermost coals of the Bowen Basin and those of the Gunnedah Basin, to the south, were thought to be of the same age, but palynological evidence has shown that the coals of the Gunnedah basin are considerably older (see Korsch et al. 1997).

The absence of coals has also been used by Veevers (1994), and others, to mark the base of the Triassic; but without supporting palaeontological evidence this assumption is, of course, not always correct.

In summary, the lithological criterion reflects a change in process, which may or may not be time significant. Certainly there was, at least initially, no other supporting evidence to support a basal Triassic age for the sediments immediately overlying the coalmeasures in eastern Australia. In the Perth and Carnarvon basins of western Australia there is a significant time break between the uppermost Permian and the overlying Early Triassic, which is dated by marine faunas (see below).

PALAEOONTOLOGICAL EVIDENCE

Global criteria

As originally defined, the upper boundary of the Permian System was coincident with the top of the Tatarian Stage of the Russian Platform (see Gomankov 1992; Fig. 2). The base of the Triassic was initially defined in Germany and recognised on lithological criteria. Both the Upper Permian and Lower Triassic sections are predominantly of non-marine origin, and correlation is possible only using plant microfossils. But the full potential of this microfossil group for international correlation is yet to be realised; it is hampered by the lack of systematic study of palynofloras from the respective type sections (but see Visscher 1980; Visscher & Brugman 1981, 1988) and apparent parent plant provincialism (Gomankov et al. 1998 for discussion). Historically plant microfossils are relatively new agents for correlation, and so marine megafossils were first to replace lithological criteria for correlation. As a consequence, marine equivalent sections for the uppermost Permian and basal Triassic were established in Europe, North America and Asia.

In 1997, the Subcommittee on Permian Stratigraphy proposed to select formally stratotypes for the Upper Permian units of the Standard Global Chronostratigraphic Scale from outside Russia (Jin et al. 1997). The Changhsingian, from the Meishan region of China, is proposed as the uppermost stage of the Permian, replacing the Tatarian. This is a carbonate dominated section with well documented marine faunas, particularly conodonts, and other fossil groups, including spores and pollen (although recovery of these fossils can be difficult).

The incoming of the conodont *Hindeodus parvus* is proposed to mark the boundary of the Early Triassic (Yin et al. 1996). Although this is the currently accepted criterion, its use has come under intense international scrutiny. These concerns, however, are largely academic, because at present *H. parvus* is unknown from Australia, or indeed from any other currently Southern Hemisphere Gondwanan deposits. Thus the primary faunal criterion for recognition of the basal Triassic cannot be applied to Australian deposits; correlation must be achieved using other faunal groups.

Australian marine fauna

The youngest Permian marine faunas of Dzhulfian age occur in the Canning Basin of Western Australia (Archbold 1998). Faunas of Changhsingian age have not been recognised. Ammonites and

bivalves from the Kockatea Shale of the Perth Basin, Western Australia, provide links with the Early Triassic, and are of late Greisbachian in age (see McTavish & Dickins 1974). These are the faunal anchor points for the Australian Late Permian and Early Triassic.

Floral evidence

Balme (1962) considered that the range of the distinctive Gondwanan *Glossopteris* Flora spanned the Permian Period; as a consequence the demise of the Flora marked the P-T boundary in Australia. As an extinction event, it could be assumed to be coincident and consistent with the extinction of the marine fauna throughout much of the global Permian (see Erwin 1993). Such an assumption, however, involves circular arguments and accepts that extinction rates between floras and faunas are synchronous, a view not supported by all workers (see Traverse 1988).

The last glossopterids seem to occur within the uppermost Permian coalmeasures of eastern Australia, and so placement of the P-T boundary on lithological grounds (see above) was apparently supported by local floral evidence. The palynological expression of the *Glossopteris* Flora, particularly characterised by striatitid pollen, was used by Balme (1969), Evans (1969), and all subsequent workers, to further refine the placement of the P-T boundary.

Palynology. International correlation using palynomorphs, despite the problems mentioned above, was achieved between Australia and Pakistan following Balme's (1970) study of the Salt Range sections. Balme & Helby (1973) established correlation between palynofloras from the uppermost Chhidru Formation (currently regarded as early Changhsingian) and those from immediately overlying the uppermost coalmeasures of the Sydney Basin in eastern Australia (see Fig. 2).

Foster (1979) found correlative palynofloras at the base of the uppermost coalmeasures in the Bowen Basin, which showed that quantitatively small but significant palynofloral change had occurred prior to the end of coalmeasures sedimentation. The first appearance datum (FAD) of *Triplexisporites playfordii* and *Playfordiaspora cancellosa* (al. *crenulata*) are keys to correlation. In Australia, the FAD of *T. playfordii* is a key temporal marker (Fig. 3). In eastern Australia, it appears in coalmeasures where the parent plant was part of the swamp flora; the same palynospecies continues to flourish in redbeds in both eastern

and western Australia, and makes its last appearance in the Late Triassic. As emphasised by Foster & Jones (1994), correlation with the Salt Range section is dependent on the known range of *T. playfordii* and the other key species (see list in Foster 1982). At present it is known only from the uppermost Chhidru Formation (Unit 4), but only from study of relatively few samples (11, see Balme 1970). More extensive sampling and study is needed urgently. Migration of the parent plants presumably occurred during global lowstand, and it has been assumed that the FAD of the key spore-pollen species is synchronous, within some degree of unresolvable error. This assumption needs testing because the physical processes to preserve both the sediments and palynomorphs, and in particular the creation of accommodation space, must occur after the original migration and involve at least one other local migratory phase as the parent plants adjust to the subsequent transgressive event.

The 'fungal' connection. Above the uppermost coals of the Bowen Basin, in the overlying Rewan Formation, Foster (1979) described and named large fungal-shaped palynomorphs as *Chordecystia chalasta* (Fig. 4). Closely comparable taxa were described later in the same year by Balme (1979) from Permian-Triassic sediments of Greenland as *Tympanicysta stochiana*. These taxa may be conspecific, although European examples show a broader range of morphologic variation. Visscher et al. (1996) have gone further to suggest that both these genera belong to *Reduviasporonites* Wilson 1962 first described from the Permian of Oklahoma. From Foster's study of the Oklahoma type material, and assemblages from Australia, Greenland, Britain and Russia, the synonymy of Visscher et al. is not followed. Despite this, the widespread occurrences of these forms in Europe, China (Meishan section), Israel and Australia has led to the concept of a 'fungal spike' (Visscher et al. 1996; Eshet et al. 1995; Wood & Mangerud 1994) to mark the close of the Permian (Fig. 5).

The scenario is attractive, as these forms are seen to flourish in a decaying and doomed global ecosystem where faunal extinctions, at least, reach 90% (Erwin 1993). However the records of *C. chalasta* from Kazanian assemblages from the Russian Platform, some 17 Myr before the P-T boundary, suggest that these taxa are a disaster species which bloom opportunistically (see Foster et al. 1997). As such they mark an ecology, rather than a synchronous and unique event. The biological affinities of the microfossils remains speculative; but a fungal origin is suggested because

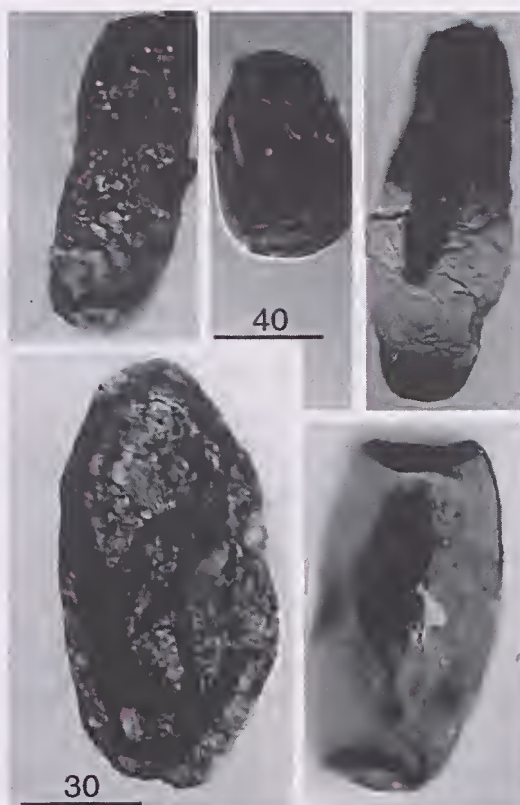


Fig. 4. Australian Late Permian *Chordecystia chalasta* Foster 1979: 1, 3, topotype material from the Bowen Basin, Queensland (scale bar 30 μ m); 2, 4, 5, examples from the Bonaparte Basin, northern Australia (scale bar 40 μ m).

they look like modern forms, although their size range is approximately 10 \times that of recent and fossil fungi.

PROXIES FOR THE P-T BOUNDARY

Non-palaeontological and non-lithological criteria for placement of the P-T boundary in Australia include: numeric age dating of single zircon crystals recovered from tuffs, using the Sensitive High Resolution Ion Microprobe (SHRIMP); and the use of shifts in carbon isotopic composition determined from organic matter or kerogen. The results of each are reviewed below.

Radiometric dating—SHRIMP

Single zircon crystals from various tuff horizons from the P-T boundary section at Meishan have

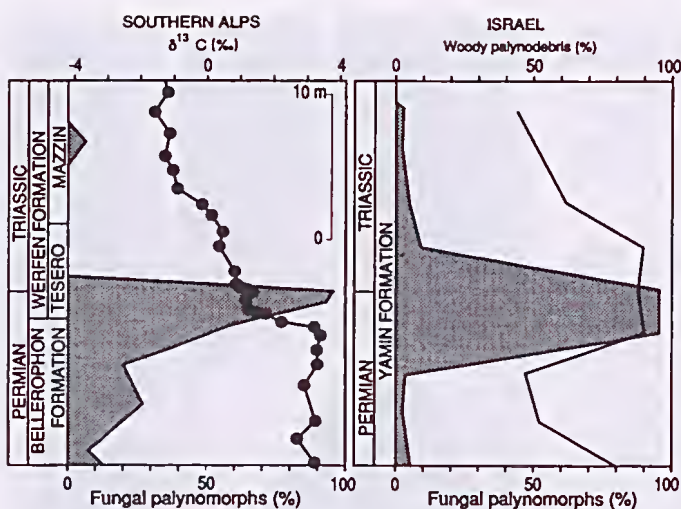


Fig. 5. Carbon isotopes (from carbonates), percentages of woody debris and fungal remains (as in Fig. 4), from two key boundary sections in the southern European Alps and Israel (after Visser et al. 1996).

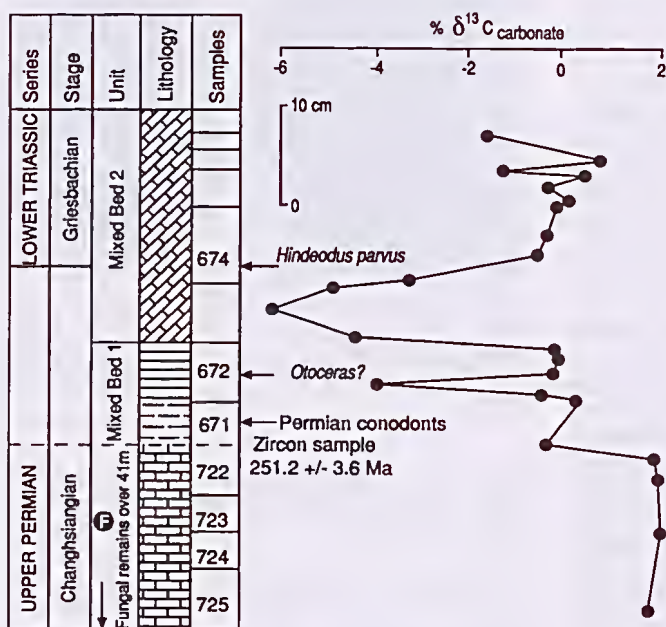


Fig. 6. Fauna, carbon isotopes (from carbonates), and SHRIMP samples from the proposed Permian-Triassic global stratotype section (D) at Meishan, China.

been dated by the SHRIMP technique. The first date from the so-called boundary clay was given as 251.2 ± 3.4 Ma (Claoué-Long et al. 1991, 1995). Yin et al. (1992) have provided a comprehensive account of the nature of the boundary clay rock from many localities across southern China. Fig. 6 shows the section containing the dated tuff layer, considered originally as the 'boundary clay' or 'White Clay', at the boundary between the Permian Changhsing Formation and the Triassic Chinglung Formation (see also Xu & Yan 1993;

Yin 1996). Subsequent work at Meishan has shown that this tuffaceous layer contains a Permian conodont fauna, and occurs approximately 14–15 cm below the first appearance of the conodont *H. parvus* (Yin 1994).

The initial date has been refined by subsequent SHRIMP work on the same tuff at Section D (Bed 25 of Yin et al. 1996) at 252.6 ± 1.0 Ma, and zircons from a tuff in Bed 35, 7.3 m above Bed 25, were dated at 252.4 ± 1.2 Ma (Metcalf et al. 1997): which essentially is the same date.

The P–T boundary is therefore taken as 252.6 ± 1.0 Ma. Bowring et al. (1998) have also dated the Meishan sections, with samples from Sections A to D and Z. Of particular interest are dates from Section D for the Permian lower part of the Changhsing Formation dated by isotopic dilution techniques at 253.4 ± 0.2 Ma (approximately 30 m below the P–T boundary—see Bowring et al.: fig. 2), and the Early Triassic Bed 33 (2.25 m above the P–T boundary) at 250.4 ± 0.5 Ma. Although not determined from ash beds at Section D, the proposed stratotype, Bowring et al. place the boundary at 251.4 ± 0.3 Ma, slightly younger than the SHRIMP age reported by Metcalfe et al. 1997.

In Australia, Roberts et al. (1996) reported a SHRIMP date of 250.1 ± 2.8 Ma for a tuff in the Black Alley Shale, underlying the Baralaba Coal Measures in the Bowen Basin (Fig. 3). Accepting the validity of the Meishan data, the Black Alley Shale is of Triassic age, as are the overlying *Glossopteris*-bearing coal measures (but see above). Are the dates from the Black Alley Shale in error? Draper & Fielding (1997) argued that this date is inconsistent with other SHRIMP dated horizons in Queensland (cf. Roberts et al. 1997). Another possibility is that variation in the standard (or reference) zircon, SL13 (Compston 1996), used in dating the Black Alley, but not the Meishan samples of Metcalfe et al., may explain these differences in age.

When comparing Early Palaeozoic ages determined by SHRIMP and by isotope dilution techniques, Tucker & McKerrow (1995: 372) suggested that SHRIMP ages 'are too young because of a minor bias of ~1–2% in the SHRIMP calibration ...'. Applying such a correction factor to the Black Alley Shale its age may be between 252.6 and 255.1 Ma. But this is speculation, and it is clear that the Black Alley Shale, and other tuffs below the coal measures, must be re-dated, and this is currently in progress.

However, assuming that the older date of 252.6 Ma is correct for the Black Alley Shale, and that is within the Triassic, how does this fit with other palaeontological evidence? The palynoflora from the Black Alley Shale belongs to the *Dulhuntyispora parvithola* Zone. In the Canning Basin of Western Australia, palynofloras belonging to this zone are considered to be, at least in part, of Dzhulfian (Late Permian) age, dated by faunas in correlative beds of the Liveringina Group. It should be noted that the fauna, including the ammonoid *Cyclolobus*, is recovered from ferruginised surface rocks of the Hardman Formation and that the palynomorphs are recovered from subsurface beds

close to the type section of the Hardman Formation (see Backhouse 1998). This is evidence at least of a Late Permian age for the *D. parvithola* assemblages. Palynofloras from the Kockatea Shale, dated by bivalves and ammonites as late Early Triassic (late Greisbachian—see McTavish & Dickins 1974), belong to Dolby & Balme's (1976) *Kraeuselisporites saeptatus* Zone. Key elements of the zone include lycopod spores of *K. saeptatus* and *Densoisporites* spp., and as shown by Foster (1982) and De Jersey (1979) these key elements occur in palynofloras recovered from the Rewan Formation, which overlies, either conformably or unconformably the coal measures, which in turn overly the Black Alley Shale. Put more simply, Early Triassic palynofloras from eastern Australia occur hundreds of metres, in section, above the tuffs of the Black Alley Shale.

For this paper it must be concluded that SHRIMP dating does not currently allow recognition of the P–T boundary in Australia.

CARBON ISOTOPES FROM CARBONATES AND ORGANICS

Overview

Global carbon isotopic signatures from carbonates ($\delta^{13}\text{C}_{\text{carb}}$) which span the Permian–Triassic boundary show a sharp shift, the Triassic carbonates being 4 to 5‰ lighter than those from the Permian (Figs 5, 6). Baud et al. (1989) and subsequent investigators (Chen et al. 1991; Xu & Yan 1993; Morante et al. 1994; Knoll et al. 1996) used these changes to correlate between key global sections. Scholle (1995) reviewed the data used for correlation, and noted that secular variation in both carbon and sulphur isotopic composition occurred, but that diagenetic problems complicated the picture (see also Oberhänsli et al. 1989). Scholle (1995: 144) concluded that 'the establishment of a secular variation curve which has enough detail and reliability to be used as a chemostratigraphic tool still lies in the future'.

Any secular variation in $\delta^{13}\text{C}_{\text{carb}}$ should also be apparent in $\delta^{13}\text{C}$ signature of total organic carbon ($\delta^{13}\text{C}_{\text{org}}$) where present.

Morante and co-workers provided a comprehensive set of $\delta^{13}\text{C}_{\text{org}}$ values for a number of wells from both eastern and western Australia (Morante 1995; Morante et al. 1994; Morante & Herbert 1994). From this data set they have suggested that isotopic shifts of a similar magnitude, from –4 to –8.5‰, provide 'an isochronous global datum in the sedimentary record at the palaeontologically defined Permian–Triassic boundary' (Morante et al.

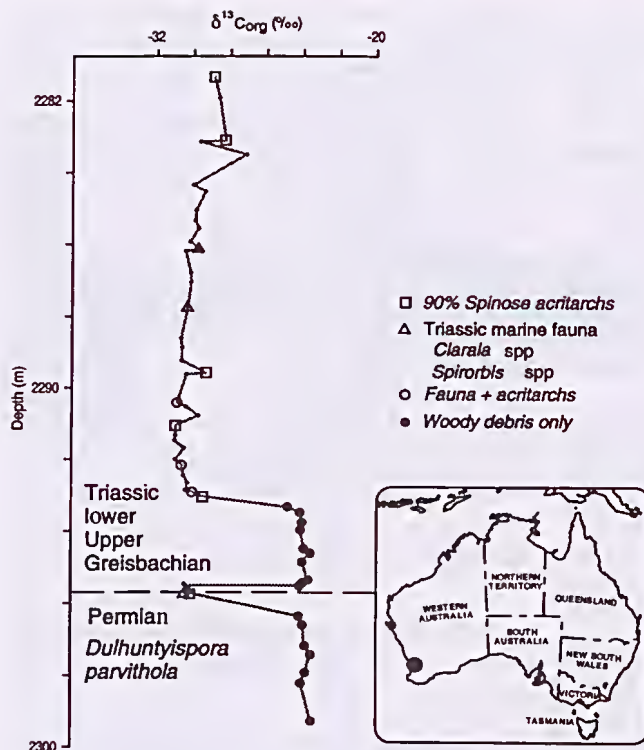


Fig. 7. Carbon isotopic signature from core 1, Woodada-2, Perth Basin. Permian sediments dated by plant microfossils. The peak at 2295.88 m coincides with the first appearance of the bivalve *Claraia* sp. and indicates an Early Triassic age.

1994); and further, that isotopic chemostratigraphy has application for both intrabasinal and global correlation (e.g. Retallack 1996). As a result of more recent work, Foster and co-workers considered that carbon isotopic signatures are affected by secular change, but more importantly may be overprinted by contributions from different organic sources or facies (Gorter et al. 1995; Foster et al. 1997; see also Xu & Shen 1989). As a consequence, this criterion cannot be used for precise dating.

Carbon isotopes in Australia

The key question is whether the secular changes in carbon isotopic composition can be isolated from the other causes of changes in isotopic value. As noted above, Scholle (1995) drew attention to the masking and contributing effects of diagenetic processes to the determination of carbon isotopic values from carbonates. For organic matter, issues affecting the carbon isotopic composition are complex and include physiological, environmental and taxonomic factors (e.g. Falkowski 1991; Lloyd & Farquhar 1994) as well as any secular contribution (e.g. Tieszen 1991; Rau 1994).

Foster et al. (1997) have summarised their studies in the Perth, Bowen, Bonaparte and Sydney basins and showed that kerogen composition was closely correlated with the observed shift in carbon isotopic values. In particular, where woody tissue was present in relatively low proportion, as determined by standard visual kerogen analysis, the sample was isotopically light (Gorter et al. 1995). This pattern has now been observed in a number of wells and a model to determine the relative contribution of end-member organic matter types, using isotopic signatures of either kerogen or oils has been discussed by Foster et al. (1997). Some of their findings are summarised below.

Perth Basin

Woodada-2, core 1. This core was originally considered as a potential Permian–Triassic boundary section, and shows variation in organic matter input as well as $\delta^{13}\text{C}$ of kerogen (see Gorter et al. 1995). The occurrence of the bivalve *Claraia* throughout much of the core provides independent evidence of an Early Triassic age (Fig. 7). The base of the core has been dated as Late Permian, based on palynological evidence (see Gorter et al. 1995).

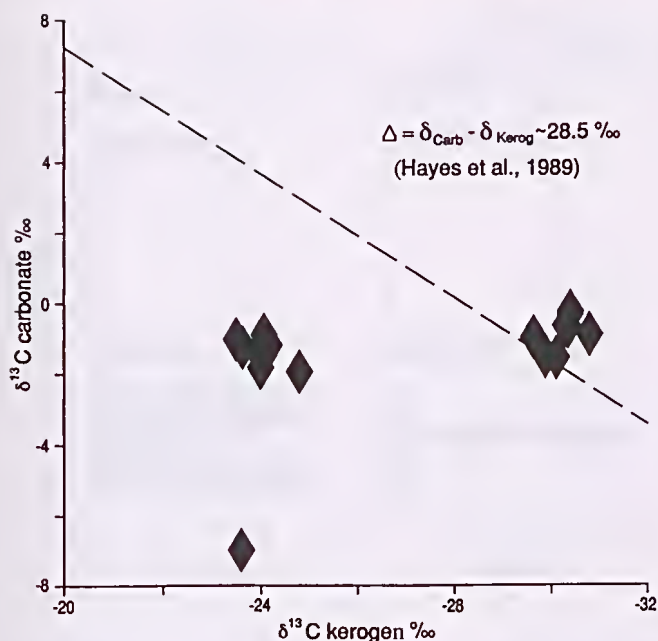


Fig. 8. Isotopic cross-plot of kerogen and carbonate from the Woodada-2 core. Kerogen of around -30‰ , derived from Triassic horizons shows a isotopic relationship with co-existing carbonate with an isotopic separation of 28.5‰ , suggesting a primary relationship of both. Kerogen $\delta^{13}\text{C} -24\text{‰}$ from both Triassic and Permian horizons does not plot on the line and indicates that the carbonate and kerogen do not both have a primary origin in the same water column.

The $\delta^{13}\text{C}$ profile shows that typical 'Permian' values of -24‰ occur in the Triassic; the remainder of the Early Triassic is isotopically lighter, from -27.18 to -31‰ . High concentrations of woody tissue are associated with kerogen enriched in ^{13}C (see Gorter et al. 1995, table 1, for details). In the 1995 study we concluded, on available evidence, that reworking had not contributed to high concentrations of woody debris found in the Triassic samples. This conclusion is overturned by new studies of carbon isotopes from associated carbonates and by evidence from Rock-Eval pyrolysis.

Carbon Isotopes from Associated Carbonate—Woodada-2. Where primary carbonate and organic matter are formed in the same water column, a kinetic $\delta^{13}\text{C}$ isotope effect exists which causes organic matter to be depleted by about 28‰ , compared to carbonate (Hayes et al. 1989). For the Woodada-2 core, a cross-plot of carbonate and kerogen (Fig. 8) shows that organic matter with an isotopic composition of $\sim -30\text{‰}$ plots on a line linking kerogen and carbonate pairs at $\sim 28.5\text{‰}$, as predicted by the model of Hayes et al. (1989). However, carbonate associated with wood-dominated kerogen (-24‰) does not plot on this line (Fig. 8). A decoupling of the kerogen-carbonate relationship occurs due to the influence of

terrestrially-derived woody tissue on the overall isotopic composition of the kerogen. These data alone have implications for the uses of chemostratigraphy in the correlation of Permian and Triassic sections, since the terrestrial influence on the isotopic composition of kerogen is not a local phenomenon but occurs in other basins, and during different geological periods.

Given that the controlling factor on isotopic composition of the Woodada-2 kerogen is the variation in contribution of organic matter types, and that we have good estimates on the isotopic composition of the terrestrial and marine end-members, it is possible to use the observed data to calculate the proportion of marine and terrestrial organic matter, based on the isotopic composition of the bulk kerogen, using the following formula modified from Jasper & Gagosian (1990):

$$F_t = (\delta^{13}\text{C}_s - \delta^{13}\text{C}_m) / (\delta^{13}\text{C}_t - \delta^{13}\text{C}_m)$$

F_t = fraction of C_{org} that is terrestrial
 $\delta^{13}\text{C}_s = \delta^{13}\text{C}_{\text{org}}$ of a given sample
 $\delta^{13}\text{C}_t = \delta^{13}\text{C}_{\text{org}}$ of the woody tissue end-member
 (= -24‰)
 $\delta^{13}\text{C}_m = \delta^{13}\text{C}_{\text{org}}$ of the marine acritarch-rich end member
 (= -30‰)

From the above calculation, a model was derived relating the variation of organic matter input to

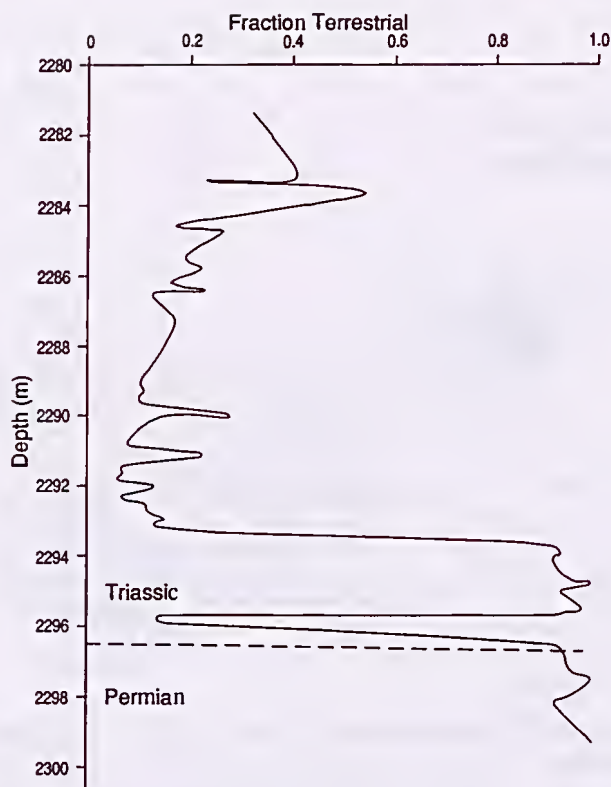


Fig. 9. A model of the fraction of terrestrially derived material in the Woodada-2 core based on the isotopic composition of the kerogen and known end-members.

marine and terrestrial influence (Fig. 9). This model curve can be read in the same way as a sea-level curve, with high levels of terrestrial influence associated with regressive low sea-level stands, and low terrestrial influence associated with transgressive high-stand systems.

Rock-Eval Pyrolysis—Woodada-2. Further work on the Woodada-2 core used this standard technique for the assessment of hydrocarbon potential and organic maturity (cf. T_{max} values). Fig. 10 shows that the wood-dominated kerogen from the Permian and Early Triassic have T_{max} values of about 485°C , and that the acritarch-rich kerogen (Early Triassic) is associated with values about 435°C . A difference of $\sim 50^{\circ}\text{C}$ in samples derived from within a few metres of each other indicates that the woody tissue is most likely to have been reworked from thermally mature sediments of the hinterland. This value is too great to be attributed simply to differences in the reaction kinetics of different types of organic matter (cf. Foster et al. 1986).

Hydrocarbons—Woodada-2. The influence of woody tissue on the kerogen also extends to hydrocarbon yield. Kerogen rich in acritarchs yields an order of magnitude more extractable organic matter (EOM) compared to kerogen rich in woody tissue (Fig. 10). This result is not unexpected, since the hydrocarbon yield from lignin-rich organic matter is likely to be less than that from aliphatic biopolymers produced by certain algae. This has important implications for petroleum generation and source rock potential within the basin, given that the total organic carbon (TOC) content of these samples is similar. The data outlined above indicate that the source rocks of greatest potential will contain acritarch-rich organic matter with a bulk isotope composition of about -30‰ . Kerogen with significant inputs of woody tissue will suffer a dilution effect and will yield proportionally less hydrocarbon; its isotopic composition will also exhibit an enrichment with increasing input.

Analysis of the saturated hydrocarbons was undertaken using gas chromatography (GC) and gas chromatography–isotope ratio mass spectrometry (GC–IRMS). Two distinct hydrocarbon profiles

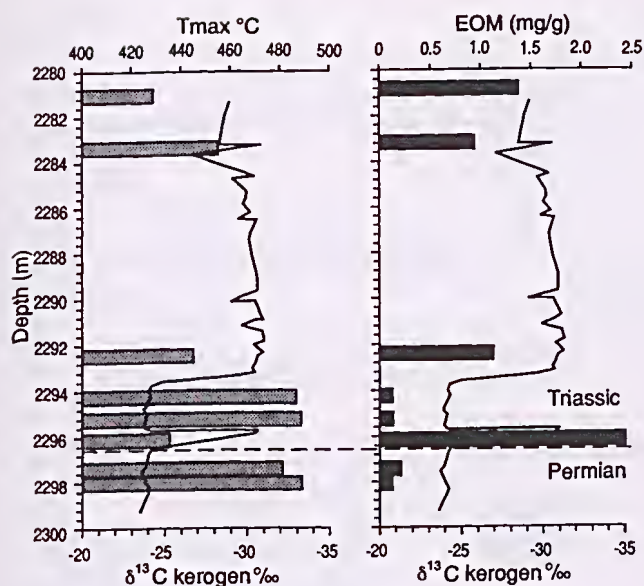


Fig. 10. Tmax and extractable organic matter (EOM) yield from Woodada-2 superimposed on the isotopic composition of the kerogen. Wood-rich kerogen has a $\delta^{13}\text{C}$ value of about -24‰ , low EOM yields and high Tmax, about 485°C . Acritarch-rich kerogen has an $\delta^{13}\text{C}$ isotopic composition of about -30‰ , much higher EOM yield, and Tmax of about 435°C . The difference in Tmax suggests that the wood has been re-worked from a thermally mature source.

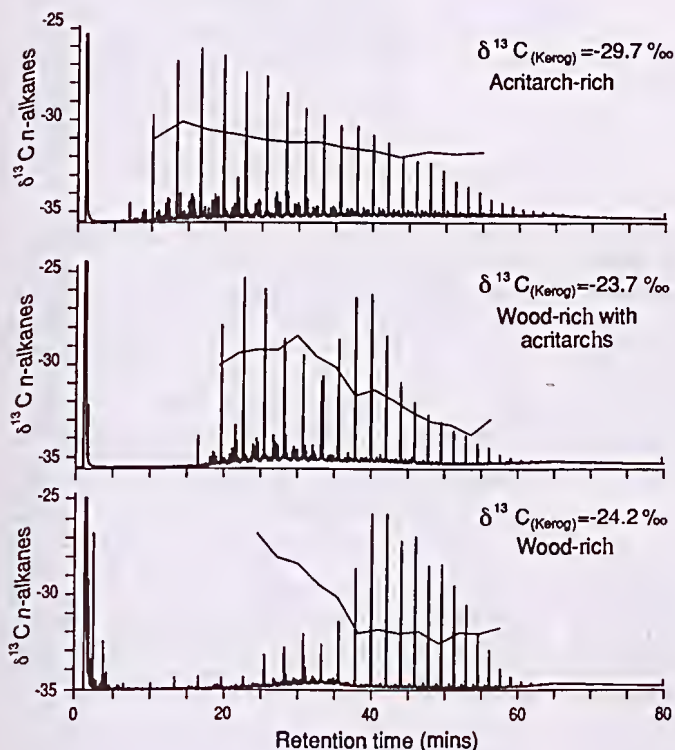


Fig. 11. GC traces of extracted bitumen from Woodada-2 and superimposed isotopic fingerprints of individual n -alkanes from these samples. The wood- and acritarch-rich kerogen form end-members, the bimodal pattern of the mixed kerogen also displaying a mixed isotopic composition.

were observed and these were also correlated to kerogen type (Fig. 11). Woody kerogen, with a low EOM, has a waxy n -alkane profile with

a unimodal distribution maximising around C_{23} . Kerogen rich in acritarchs has a much higher EOM yield, and the n -alkane profile is unimodal

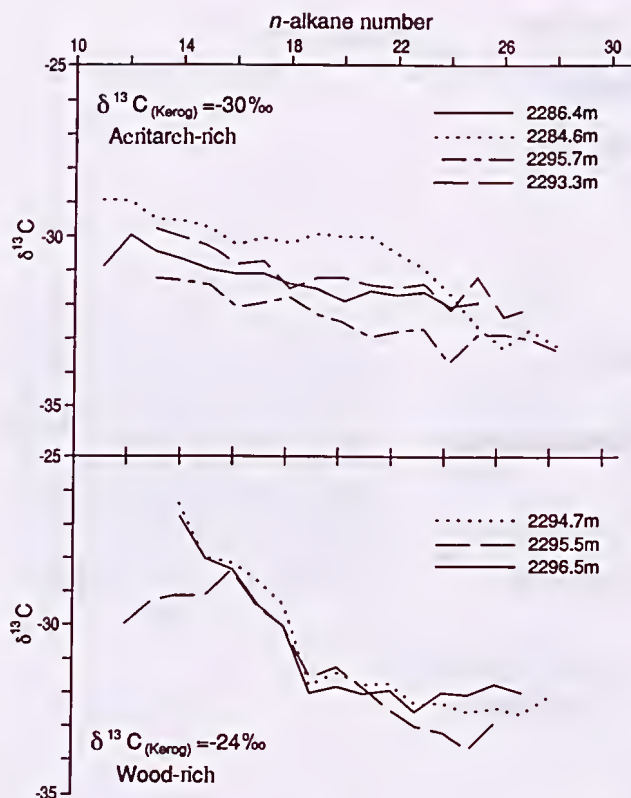


Fig. 12. Graphs of the isotopic composition of individual *n*-alkanes from bitumen extracted from Woodada-2 grouped by kerogen composition. Two distinct patterns can be seen showing the different isotopic fingerprints and their relationship to source. One sample from a wood-rich kerogen, 2295.5 m, also contains acritarchs and the isotopic fingerprint reflects this mixed kerogen source.

(maximising around C_{13}), with a much lower proportion of waxy hydrocarbons. One sample, at 2295.5 m, has a bimodal *n*-alkane distribution maximising at C_{15} and C_{23} , suggesting a mixed organic source for the bitumen. Kerogen analysis confirms an admixture of woody debris (dominant) and some acritarchs (Gortler et al. 1995). The low EOM yield from this sample is explained by the low generation potential of the woody tissue which forms the bulk of the kerogen.

Compound Specific Isotope Analyses (CSIA)—Woodada-2. Compound specific isotope analysis (CSIA, i.e. GC-IRMS on the individual *n*-alkanes) was carried out according to methods described by Freeman (1991) and Merritt et al. (1994), and has previously been applied to oils from the northern Perth Basin (Summons et al. 1995) as a correlation tool. Analysis of the saturated hydrocarbon fractions from Woodada-2 followed a trend similar to that outlined above: two distinct isotope profiles are identified and related to source facies (Figs 12, 13). *n*-Alkanes associated with acritarch-rich kerogen are also isotopically light. A minor

depletion of generally less than 2‰ with increasing chain length over the range of C_{14} – C_{28} is observed, all the profiles showing similar trends. By contrast, lower molecular weight hydrocarbons extracted from woody kerogen are enriched in ^{13}C with the isotopic composition of the C_{14} *n*-alkane near -26‰. With increasing chain length, up to C_{19} , the *n*-alkanes become increasingly isotopically depleted, reaching -32‰. This profile is clearly different from that generated from bitumen associated with acritarch-rich kerogen. The bitumen with a bimodal *n*-alkane pattern also generated a mixed isotope profile (Figs 12, 13). The lower molecular weight homologues appear to be derived from both acritarch and woody tissue types, although the isotopic composition of the kerogen is dominated by that of the woody tissue. This is because the acritarch tissue can generate an order of magnitude more extractable organic matter than the woody tissue, and thus has a much greater influence on the bitumen despite its low abundance in the kerogen. The distinct isotope profiles related to kerogen type is good evidence that the bitumen is indigenous and that staining or migration has not occurred. This is important as these isotope

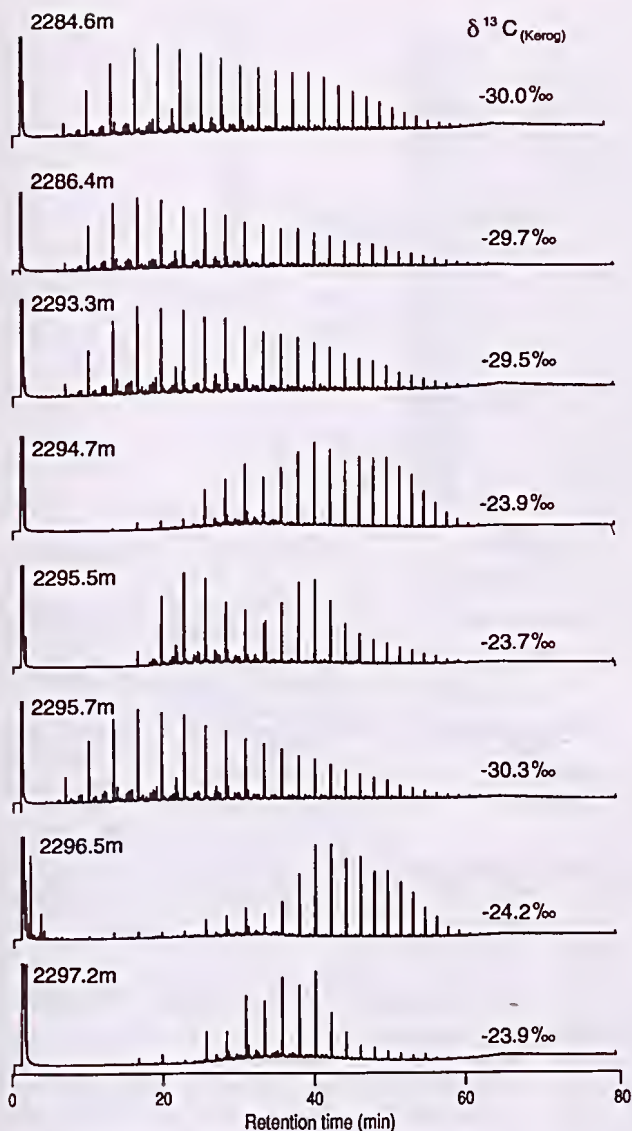


Fig. 13. GC traces of different bitumens extracted from the Woodada-2 core. Acritarch-dominated kerogen has an $\delta^{13}\text{C}$ value around -30‰ and bitumen with a unimodal pattern of n -alkanes maximising around C_{13} – C_{14} . Bitumen associated with wood-rich kerogen with $\delta^{13}\text{C}$ values around -24‰ is much more waxy, showing a predominance of higher molecular weight n -alkanes. However, one sample shows a bimodal n -alkane distribution (2295.5m) suggesting a mixture between the wood- and acritarch-rich end-members. This kerogen from this sample is predominantly woody but does contain acritarchs.

profiles can now be used as source signals that can be correlated with petroleum in the region (see below).

Bonaparte Basin-1

Tern-3. Assessment of quantitative kerogen data (Helby 1983; Foster et al. 1997) and $\delta^{13}\text{C}$ of kerogen in Tern-3 shows a significant link (90% correlation coefficient) between woody tissue and enrichment in ^{13}C (Fig. 14). Where woody tissue

is abundant, isotopic values of -24‰ are common, but as the concentration of wood decreases and the percentage of non-woody debris (e.g. acritarchs) increases, the isotopic composition shifts towards -30‰ . As noted above, a shift of -8‰ had been used to mark the Permian-Triassic boundary in this well (Morante et al. 1994). However, as in Woodada-2, it is evident that the shift is not caused solely by secular change, but is related partly to changes in the type of organic matter contributing to the kerogen. Similar isotopic changes have been

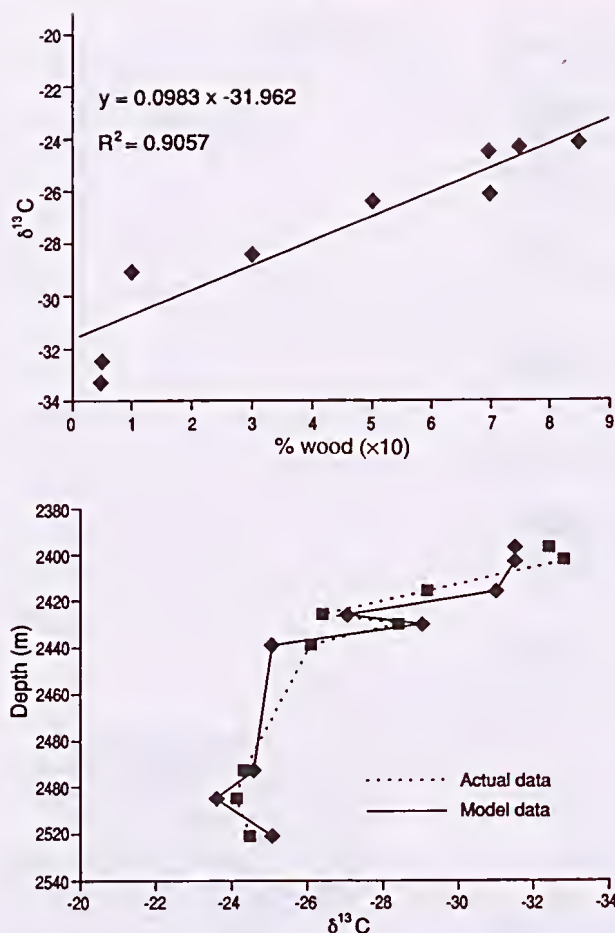


Fig. 14. Cross plot of the percentage of woody derived debris in Tern-3 samples against $\delta^{13}\text{C}$ composition of the kerogen. The straight line relationship and correlation coefficient of 0.9 shows the close correlation. The lower graph shows the actual data against that generated by using a two end-member mixing model. The close correspondence of the two graphs indicates the controlling factor in the $\delta^{13}\text{C}$ isotopic composition of the Tern-3 samples is the type of organic matter which now forms kerogen.

noted in Holocene sediments where variation in $\delta^{13}\text{C}$ is affected by input of either terrestrial or marine organic carbon (Parker et al. 1972; Newman et al. 1973).

To test the validity of these observations Foster et al. (1997) constructed a model isotope curve for Tern-3 based on the isotopic compositions of different organic sources and their known quantitative abundance (determined from palynological counts). If the model curve fits the observed data it confirms the effects of organic matter type on isotopic composition. Conversely, if organic matter type does not influence isotopic signature, the model curve will vary significantly from the observed data. Calculation from Fig. 14 indicates the two end-member kerogen types, gives respective values of -22.1‰ (woody) and -32.0‰ (acritarchs). Using these values and the proportion of each end member based on the palynological counts, the model was constructed with the following formula:

$$\delta^{13}\text{C}_{\text{model}} = F_t \cdot \delta^{13}\text{C}_{\text{wood}} + F_m \cdot \delta^{13}\text{C}_{\text{acritarch}}$$

$$F_m = (1 - F_t)$$

F_m = fraction of kerogen that is marine-derived

F_t = fraction of kerogen that is terrestrially-derived

$\delta^{13}\text{C}_{\text{model}}$ = calculated isotopic composition of model kerogen

$\delta^{13}\text{C}_{\text{wood}}$ = isotopic composition of woody tissue

$\delta^{13}\text{C}_{\text{acritarch}}$ = isotopic composition of acritarch tissue

As can be seen from Fig. 14, the model data shows good correspondence to the observed values. The relatively minor variation between the model and observed curves can be attributed to several factors which include variability of other organic components not accounted for in the model, the method of kerogen estimation and identification (see Traverse 1994, for a diversity of views),

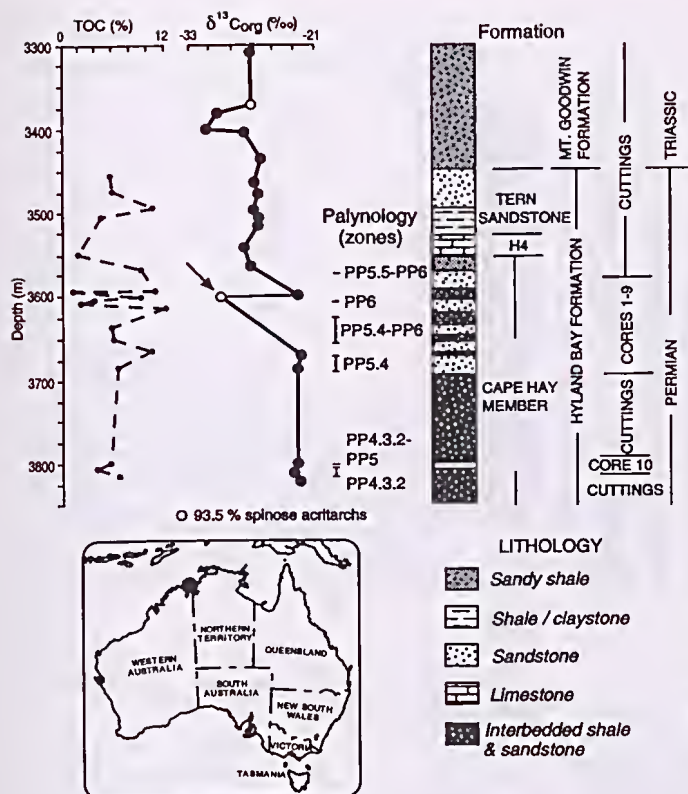


Fig. 15. Kerogen carbon isotopic signature, palynological zones and lithology from Petrel-4. Data from Morante (1995). Arrow indicates significant shift in isotopic composition in kerogen from a core sample in the APP6 zone. The assemblage is dominated by spinose acritarchs (see Fig. 16), and reflects a transgressive event.

environmental controls affecting preservation and deposition of organic matter, and secular variation in $\delta^{13}\text{C}$. Despite these variables, it is clear that the main factor controlling the isotopic composition of the kerogen in Tern-3 is organic matter type, and not the inherent age of the material. As discussed below, the combined use of palynology, isotope geochemistry, and data modelling provides a powerful tool in assessment of the value of chemostratigraphy, and points to further, novel exploration uses.

Bonaparte Basin-2

Petrel-4. Detailed carbon isotopic studies of organics from the Permian-Triassic section in Petrel-4 were reported by Morante (1995), and the palynological work was conducted by SANTOS Ltd (Wood & Benson, unpub. studies). A sample from core 4, at 3603.42 m, assigned to the *P. cancellosa* (al. *crenulata*) Zone (=APP6), shows a dramatic shift of -7.28‰ from the immediately underlying Permian (from -22.69 to -29.97‰). The lighter isotopic value is more typical of samples assigned to the Triassic (Fig. 15), and the sample

was considered to be out of stratigraphic order, or contaminated (SANTOS Ltd 1994, pers. comm.), as it is within the Permian part of the section. However, further work on core samples from Petrel-5, has shown the same anomaly, and there is now no doubt that these samples are in correct stratigraphic order. Detailed kerogen analysis shows that the Petrel-4 sample contains more than 90% spinose acritarchs, and therefore has very little input of woody debris (Fig. 16). As with Tern-3 and Woodada-2, the same influence of woody debris is evident. For Petrel-4, the light isotopic signature reflects organic input from a transgressive event. It seems, from studies by SANTOS Ltd, that the appearance of plant microfossils of the *P. cancellosa* (al. *crenulata*) Zone (APP6), at least in the Bonaparte Basin, is facies-controlled. Most importantly, we can apply the carbon isotopic values to sequence analyses (see below).

Bowen Basin

Denison NS 20. The association between kerogen type and carbon isotopic signature is also evident in the Bowen Basin. The organic carbon isotopic

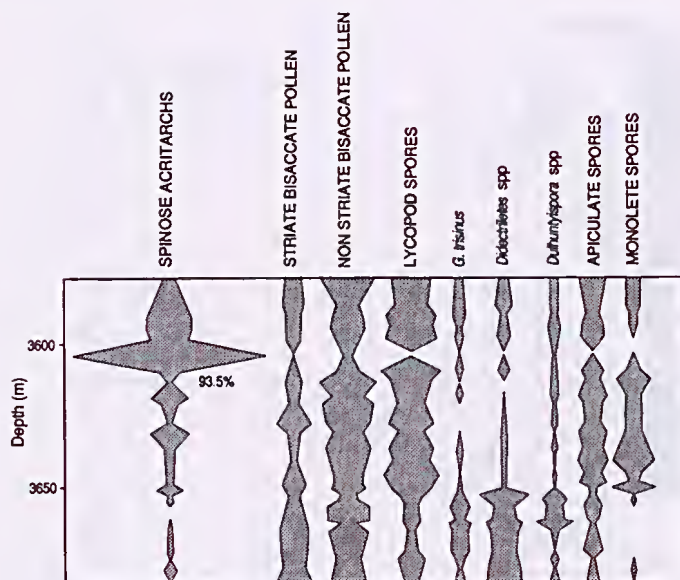


Fig. 16. Quantitative composition of plant microfossils from Petrel-4. Data from unpublished studies by SANTOS Ltd. The assemblage from the core sample at 3603.42 m is dominated by spinose acritarchs, and there is very little debris of woody origin in the assemblage. See text for further details.

profile for this well is from Morante's (1995) study (Fig. 17). In samples from the coal measures, woody debris is common; the sample from the Rewan Formation has less woody tissue, and the occurrence of spinose acritarchs, and putative fungal remains of *Chordeciystia* (see above), suggest a change in environment, with the influx of some saline waters (see Foster et al. 1997 for details).

Carbon isotopes from the Russian latest Permian and earliest Triassic

Foster et al. (1997) reported on isotopes from kerogen isolates from a surface sample from the uppermost Late Permian (Vyatsky Horizon, Tatarian Stage) of the Russian Platform (see Foster & Gomankov 1994 for locality), and from borehole cores of the basal Triassic (Induan Stage) of the Russian Pechora Basin (Yaroshenko et al. 1991) and Barents Sea (Dr L. Fefilova, VNIIOkeanogeologia, Russia, pers. comm. 1993), to determine the magnitude of any isotopic shift across the system boundary. Table 1 shows that the maximum isotopic shift is -1.79‰ . All samples are from predominantly non-marine sections, and range in thermal maturity from marginally mature to gas-condensate; maturity has not affected their isotopic composition. Woody tissue dominates all the kerogen assemblages, and, from the models developed in this paper, it is not surprising that there is such a small shift across the boundary.

On this criterion alone, the ages of the sections cannot be determined.

Age	Stage	Area	$\delta^{13}\text{C}$ -kerogen
Latest Permian	Tatarian-Vyatsky Horizon	Russian Platform	-23.57
Earliest Triassic	Induan	Pechora Basin	-25.1
Earliest Triassic	Induan	Barents Shelf	-25.26
Earliest Triassic	Induan	Barents Shelf	-24.92

Table 1. Kerogen carbon isotopes from the Russian Permian-Triassic.

Conclusions and applications for carbon isotope data

- We concur with Scholle (1995) that, while secular changes in carbon isotopic composition are evident through time, and between the Permian and Triassic, they are not well enough constrained to be used as an isochronous datum.
- Isotopic values of organic carbon seem influenced most strongly by the primary source of the organic matter, and a model has been established to predict isotopic composition from a visual quantitative assessment of kerogen components.

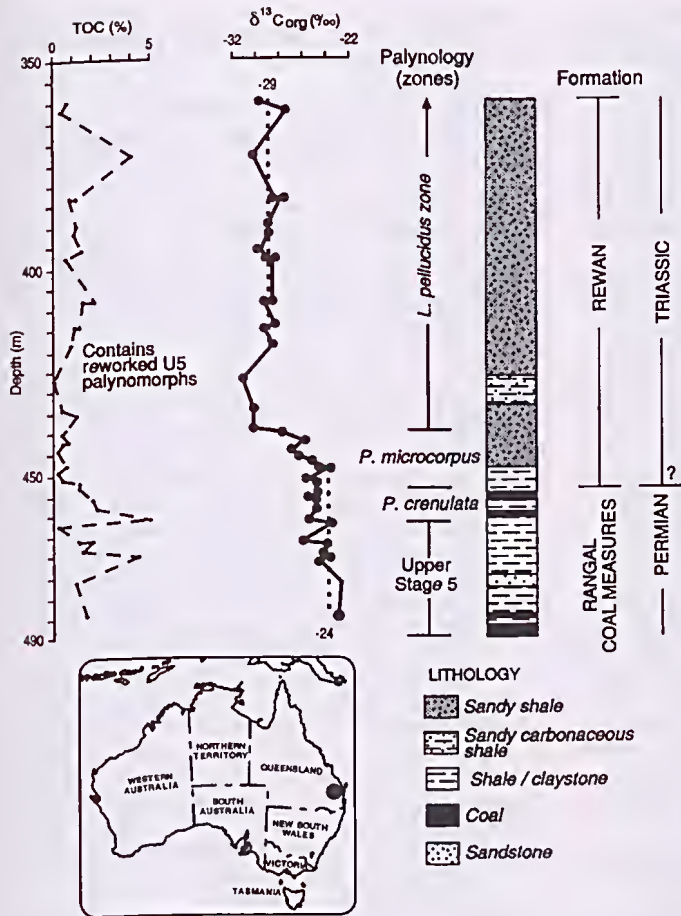


Fig. 17. Kerogen carbon isotopic composition, palynozones and lithology from a predominantly non-marine section (Denison NS 20), Bowen Basin, Queensland. Isotopic data, and position of the Permian-Triassic boundary, from Morante (1995).

CONCLUSIONS

- After 25 years, the P-T boundary in Australia remains elusive and between two palaeontological anchor points: correlation with the Late Permian (early Changhsingian) of the Salt Range uses palynological criteria from eastern Australia, and the late Early Triassic is defined by marine faunas in Western Australia.
- SHRIMP dating studies of intercalated tuffs of the eastern and south central Australian coal measures is continuing at AGSO, as is dating of tuffs from international Permian-Triassic reference sections (e.g. Meishan, China; Southern Alps, Italy; Russian Permian). At present geologic implications of early results are difficult to interpret, and questions regarding the use of an appropriate reference standard need to be resolved, before this technique can be applied to date the P-T boundary with certainty.

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